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A Bayesian approach for calculating variable total maximum daily loads and uncertainty assessment

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ABSTRACT

To account for both variability and uncertainty in nonpoint source pollution, one dimensional water quality model was integrated with Bayesian statistics and load duration curve methods to develop a variable total maximum daily load (TMDL) for total nitrogen (TN). Bayesian statistics was adopted to inversely calibrate the unknown parameters in the model, i.e., area-specific export rate (E) and in-stream loss rate coefficient (K) for TN, from the stream monitoring data. Prior distributions for E and K based on published measurements were developed to support Bayesian parameter calibration. Then the resulting E and K values were used in water quality model for simulation of catchment TN export load, TMDL and required load reduction along with their uncertainties in the ChangLe River agricultural watershed in eastern China. Results indicated that the export load, TMDL and required load reduction for TN synchronously increased with increasing stream water discharge. The uncertainties associated with these estimates also presented temporal variability with higher uncertainties for the high flow regime and lower uncertainties for the low flow regime. To assure 90% compliance with the targeted in-stream TN concentration of 2.0 mg L^{-1}, the required load reduction was determined to be 1.7×10^3, 4.6×10^3, and 14.6×10^3 kg TN d^{-1} for low, median and high flow regimes, respectively. The integrated modeling approach developed in this study allows decision makers to determine the required load reduction for different TN compliance levels while incorporating both flow-dependent variability and uncertainty assessment to support practical adaptive implementation of TMDL programs.

1. Introduction

Nonpoint source (NPS) pollution is an important cause of water quality impairment worldwide (Nyenje et al., 2010; Chen et al., 2010a), especially for eutrophication associated with excessive nutrients (Carey et al., 2011). To reduce the negative impacts of NPS pollution, control strategies such as the Total Maximum Daily Load (TMDL) program that incorporates control of NPS nutrients by watershed management, have been widely applied in many countries (Zheng and Keller, 2008; Chen et al., 2011a). However, the current pace of TMDL development is hindered due to difficulties with NPS pollution quantification and uncertainty assessment (Zheng and Keller, 2008; Freedman et al., 2008).

Many numerical models, ranging from simple export coefficient models (Johnes, 1996), to regression models (e.g., SPARROW; Smith et al., 1997), to complex mechanistic models (e.g., AGNPS, HSPF and SWAT; Borah and Bera, 2004), have been developed to estimate NPS pollution loadings for TMDL development; however, NPS pollution load estimation remains a challenge, especially because of insufficient data (Shen et al., 2006). For example, most US states lack sufficient data to quantify NPS loads, with no estimates of NPS loads for 20% of TMDLs (Freedman et al., 2008). Thus it is necessary to determine a robust method having limited data requirements for NPS pollution load estimation. The receiving stream water quality model, which links catchment NPS and point source nutrient inputs with the receiving water body quality, provides a simple and efficient tool for NPS pollution load estimation through inversely estimating the NPS pollution load from water quality and hydrologic monitoring data. The receiving stream water quality model has been increasingly applied for NPS pollution load estimation (Shen et al., 2006; Shen and Zhao, 2010; Chen et al., 2011a). However, to inversely estimate NPS pollution load by the receiving stream water quality model, it is necessary to determine the non-measurable model parameters, such as in-stream nutrient loss rate and diffusivities (Liu et al., 2008; Shen and

Abbreviations: NPS, Nonpoint source; TMDL, Total maximum daily load; LDC, Load duration curve; E, Area-specific NPS export rate; K, In-stream loss rate coefficient; RLR, Required load reduction; TN, Total nitrogen.

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Zhao, 2010). In general, these parameters have been obtained from the literature or estimated by empiristic methods, which inevitably increase the uncertainty for NPS pollution estimation (Chen et al., 2011a).

Uncertainty derived from the NPS pollution model structure, input data, and parameter estimates (Shen and Zhao, 2010) is a critical issue that requires addressing in TMDL development (Walker, 2003). Several methods have been applied for uncertainty analysis in TMDL development: first-order error analysis (Walker, 2003), Monte Carlo analysis (Shirmohammadi et al., 2006), sensitivity analysis (Arabi et al., 2007), and generalized likelihood uncertainty estimation (Stow et al., 2007). In contrast to these approaches, Bayesian statistics can evaluate the probabilistic risk of water quality management through calibrating unknown model parameters in terms of posterior joint distributions (Qian et al., 2005; Malve and Qian, 2006; Shen et al., 2006), which supports the practical adaptive implementation of TMDLs by providing an uncertainty assessment (Borsuk et al., 2003; Freedman et al., 2004). Thus, Bayesian statistics has been increasingly applied to address uncertainty in water quality modeling (Liu et al., 2008; Faulkner, 2008; Shen and Zhao, 2010; Patil and Deng, 2011). Due to optimally using information from both prior knowledge and observed data (Liu et al., 2008), determining reliable prior distributions of unknown parameters is one of the primary applications for Bayesian statistics (Malve and Qian, 2006). Commonly, prior distributions were simply assumed to be normal distributions based on the experience of watershed managers or local historical data with limited observations, which might significantly impact Bayesian modeling performance (Lee and Kim, 2008; Faulkner, 2008).

Another important concern regarding NPS pollution is variability with stream discharge volume (Shen and Zhao, 2010; Chen et al., 2011b), highlighting the requirement of considering temporal variability in TMDL development, especially for NPS pollution-dominated watersheds. The load duration curve (LDC) method, which accounts for the effects of stream discharge patterns on the load capacity, has been used for variable (i.e., flow-dependent) TMDL development (US EPA, 2006). The LDC yields variable TMDLs for different hydrologic conditions and has been used extensively by the US-EPA in recent years (US EPA, 2007). However, this method does not take into account in-stream nutrient fate and transport processes (US EPA, 2006; Shen and Zhao, 2010). If factors other than the dilution capacity influence the water quality, the LDC method becomes insufficient for variable TMDL development (Chen et al., 2011a). For example, in-stream nutrient assimilation, which often accounts for an important fraction (1–80%) of the nutrient load (Faulkner, 2008; Chen et al., 2010b), is significantly modified by stream water discharge (Smith et al., 1997; Alexander et al., 2000) and is not addressed by the LDC method.

This study addresses the limitations of current receiving stream water quality models by incorporating Bayesian statistics and LDC methods to determine variable nutrient TMDLs and associated uncertainty assessment. An existing stream nutrient model (Chen et al., 2011a) was used to relate the catchment NPS nutrient export load with stream nutrient load. Then Bayesian statistics were employed to inversely calibrate catchment area-specific NPS export rate (E) and in-stream loss rate coefficient (K) from stream measurements. A literature review for E and K was performed to obtain their prior distributions to support Bayesian parameter calibration. The resulting posterior E and K were used for posterior simulations of catchment NPS export load, TMDL (i.e., total maximum daily loading that can be exported from the catchment to the stream), required load reduction, and the uncertainty assessment associated with these estimations. The LDC method was finally used to describe the variability of NPS export load, TMDL and required load reduction. The feasibility of the proposed integrated modeling approach was demonstrated by developing a variable TMDL for total nitrogen with its associated uncertainty assessment for a typical agricultural watershed in eastern China. This integrated modeling approach combines the merits but overcomes the limits mentioned above for receiving stream water quality models. The integrated approach provides a novel tool for addressing the variability and uncertainty issues of TMDLs, while also determining the required load reductions at different water quality compliance levels to support the practical adaptive implementation TMDL programs. Importantly, the method can be implemented with limited data requirements.

2. Materials and methods

2.1. Study watershed

The ChangLe River watershed (120°35′56″–120°49′03″ E and 29°27′98″–29°35′12″ N) is located in Zhejiang Province, eastern China (Fig. 1). The ChangLe River system is one of the main tributaries of the Cao-E River, which ultimately flows into the Qiantang Estuary and East China Sea. The river system drains a total area of 864 km^2 and flows about 70.5 km with a 0.36% gradient and a 40–70 m width. The river system examined in this study contains two mainstream sites (S1, NanShan Reservoir; S7, MS, downstream boundary) and five tributaries (S2, Beijiang Creek (BJ); S3, Shanyuan Creek (SY); S4, Shihuang Creek (SH); S5, Furun Creek (FR); S6, Chongren Creek (CR)) (Table 1). The area represents a typical agricultural watershed in southeast China and is characterized by a subtropical monsoon climate. Long-term average annual rainfall is 1256 mm with the highest rainfall usually occurring in May–June and August–September. The primary land-use categories in the watershed are woodland and farmland (including paddy fields, uplands, and garden plots). Point source pollution (including wastewater treatment plants and industrial sewage outlets) is negligible, with an annual TN discharge of 0.3 Mg in 2004–2009. Water input from headwater streams released through NanShan Reservoir (S1) accounts for only 8 ± 5% of the annual cumulative discharge at S7 due to export for drinking water. Therefore downstream catchment runoff is the main water source (92 ± 7%) for the entire river system.

2.2. Basic data collection

Total nitrogen (TN) concentrations at seven sampling sites (S1 to S7) along the ChangLe River were monitored monthly from January 2004 to December 2009 (Fig. 1). Water samples for chemical analysis were collected between 9:00 and 14:00 in 2.5 L polyethylene bottles from 30 cm below the water surface from three points within the cross section at each site. Water samples were acidified with H_2SO_4 in the field (15 mL concentrated H_2SO_4 per 2.5 L sample). Total nitrogen concentration was measured within 8 h of sampling using the persulfate digestion–UV spectrophotometric method (NEPA, 2002). Instantaneous stream flow velocity and water depth were determined at three points within the cross section (25%, 50% and 75% widths) using a 2150 Area Velocity Flow Module (Isco Inc., US). The instantaneous stream discharge (Q, m^3 s^{-1}) was estimated as: $Q = \bar{v}\bar{d}(W + Z\bar{d})$, where W is riverbed width (m), Z is side slope ratio, and $\bar{v}$ (m s^{-1}) and $\bar{d}$ (m) are the average flow velocity and water depth of the three points (YSI 2150 User's Manual). The average instantaneous flow velocity of each stream was obtained from the measured data at three sites along the stream flow direction (i.e., upstream, midstream and downstream sites). Daily TN loads at each sampling site were calculated by multiplying the TN concentration by stream discharge. Continuous daily stream discharge, riverbed width (e.g., 9.01–55.0 m) and side slope ratio (e.g., 1.12–2.08) at the seven sampling sites were supplied by the Zhejiang Provincial Government Hydrology Office, China. Correlation analysis, the Kolmogorov–Smirnov test (K–S test) and the coefficient of variance (CV) were determined using SPSS statistical software (Version 16.0; SPSS Inc., Chicago, USA).

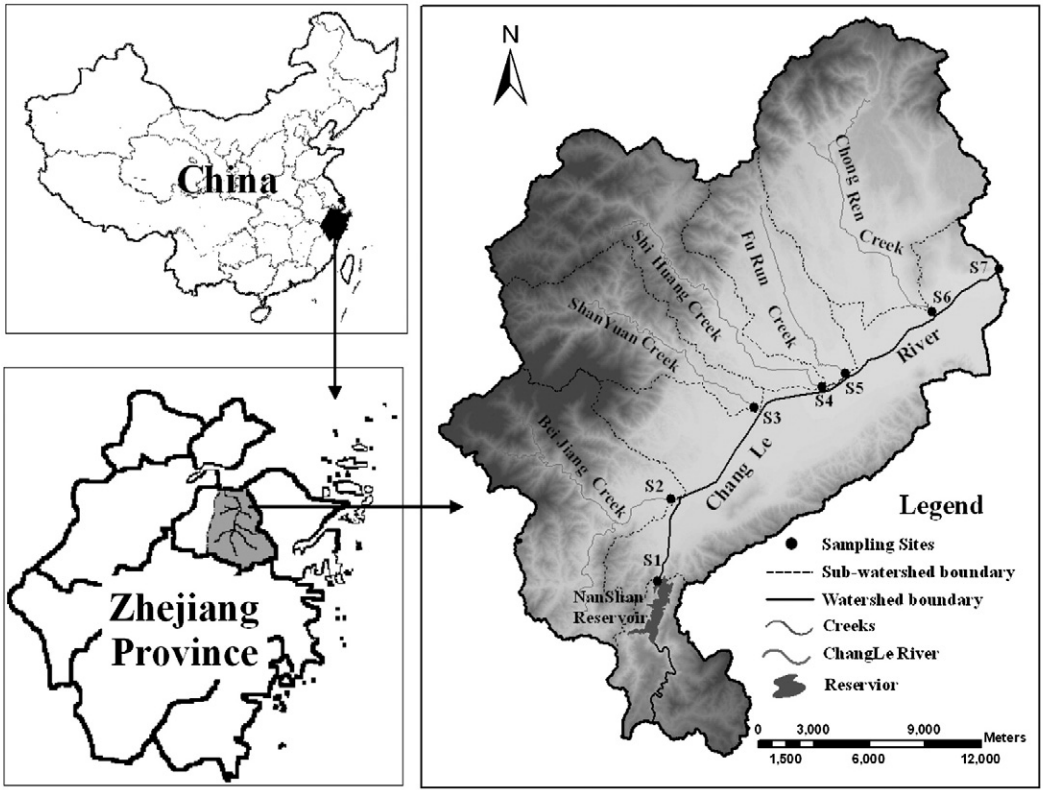

Fig. 1. Geographical location and sampling sites in the ChangLe River watershed.

2.3. Bayesian approach for variable TN TMDL development and uncertainty analysis

An integrated modeling approach that combines a receiving stream nutrient load model, Bayesian statistics and the load duration curve (LDC) method was developed for variable TMDL and uncertainty assessment with limited data requirements. This integrated modeling approach includes the following application aspects: (i) catchment NPS nutrient export load is related to stream nutrient load by a receiving stream nutrient load model, (ii) based on the prior distributions of targeted parameters in the model, selected parameters were synchronously calibrated from stream monitoring data using Bayesian statistics, (iii) the posterior catchment NPS export load, TMDL and required load reduction (RLR) were predicted along with the associated uncertainty using the posterior model parameters, (iv) the variability of catchment NPS export load, TMDL and RLR with stream discharge was expressed within the framework of the LDC method; and (v) the relationship between posterior RLR and its corresponding exceedance percentile was established to evaluate the uncertainty of exceeding the TMDL or target in-stream nutrient concentration.

Table 1
Characteristics of land-use distribution and streams in the six catchments of the ChangLe watershed in 2004–2009.

Catchments	BJ	SY	SH	CR	FR	MS
Total area (10^3 ha)	10.6	6.7	9.9	14.6	5.5	18.0
Farmland (%)	25.0	38.7	40.1	43.4	55.1	52.1
Residential land (%)	3.5	2.5	3.7	8.3	10.1	11.1
Woodland (%)	70.5	58.0	55.7	47.5	34.1	36.6
Other (%)	1.0	0.8	0.5	0.8	0.7	0.2
Population ($\times 10^3$)	30	22	11	67	30	106
Stream length (km)	17.92	16.95	33.50	24.71	18.27	27.14
Average stream discharge at catchment outlets ($m^3\ s^{-1}$)	1.82	1.14	1.69	2.49	0.94	11.85

2.3.1. The receiving stream nutrient load model

The stream TN load (L_d, kg d^{-1}) at the downstream watershed outlet can be expressed as the sum of the upstream inflow (L_u, kg d^{-1}), catchment NPS exports (assuming a simple function of catchment area (A, ha) and area-specific export rate (E, kg ha^{-1} d^{-1})), and tributaries and point source inputs (L_i, kg d^{-1}) adjusted for losses due to stream attenuation processes during downstream transport (Hoos and McMahon, 2009). In-stream TN assimilation processes are integrated as a first-order reaction based on a first-order in-stream loss rate coefficient (K, d^{-1}) and the in-stream travel time (T or T_i, d). The in-stream travel times for individual streams were calculated from the mean water velocity and flow-path length. Nitrogen entering along a given river reach within a catchment were assumed to be subject to loss over half of the stream length on average (Alexander et al., 2006). In contrast, loads entering from upstream were subject to loss over the entire stream length, and loads entering from tributaries or point sources are subject to loss over the stream length from their inlet nodes to the downstream node. As a result, for small and medium-sized streams where plug flow is much greater than dispersion, L_d can be described as (Chen et al., 2011a, 2011b):

$$L_d = L_u \exp(-KT) + EA \exp\left(-K\frac{T}{2}\right) + \sum_{i=1}^{n} L_i \exp(-KT_i). \tag{1}$$

For headwater streams or tributaries, Eq. (1) can be simplified to exclude the upstream inflow load (Hoos and McMahon, 2009).

Eq. (1) is a lumped model relating the catchment nutrient export load with stream nutrient load, comprising six measurable variables and two non-measurable parameters (area-specific export rate (E) and first-order in-stream loss rate coefficient (K)). E is the rate of TN loss to the corresponding stream per unit catchment area, representing the integrated effect of NPS TN export to the stream from N sources based on water flows or rainfall, soil types, farmland drainage volumes, land-use distributions and wetland/buffer proportions within the catchment (Johnes, 1996; Chen et al., 2010a, 2011b). K is the fraction of TN assimilated per unit water travel time, representing the integrated effect of in-stream TN loss from various physical, chemical and biogeochemical processes occurring in streams (Alexander et al., 2000; Hoos and McMahon, 2009). Based on the estimated values for E and K, catchment-scale NPS export to the stream and in-stream assimilation can be calculated from Eq. (1). As all variables in Eq. (1), with the exception of E and K, can be directly measured, E and K are the critical parameters required to describe catchment-scale nutrient fate and transport using Eq. (1).

2.3.2. Bayesian calibration for the model parameters

To estimate the catchment NPS pollution load and TMDL from area-specific export rate (E) and in-stream loss rate coefficient (K) for TN, a Bayesian approach was developed to inversely calibrate both E and K in Eq. (1). These two unknown parameters are treated as random variables with distributions derived from known information (L_d, T, L_u, L_i, A and T_i in Eq. (1)). The Bayes' theorem can be written as:

$$P(\theta/X) = \frac{P(X/\theta)P(\theta)}{P(X)} \tag{2}$$

where $P(\theta/X)$ is the posterior distribution and represents the probability of the model parameter (θ) values given the observed data (X). In our case, the parameter θ refers to E and K, i.e., $\theta=\{E_1, E_2,\ldots, E_n, K_1, K_2,\ldots, K_n\}$. $P(X)$ is the expected value of the likelihood function over the parameter distribution as a normalizing constant. $P(\theta)$ is the prior distribution, the probability density function over all values of θ prior to the observed data. $P(X/\theta)$ is the probability density function (likelihood function), which describes the mechanistic and statistical relationship between the predictor and response variables. The Markov chain Monte Carlo (MCMC) algorithm has been increasingly applied to obtain the numerical summarization of parameters (Qian et al., 2003). There are three major steps in the Bayesian model using the MCMC sampling method (Malve and Qian, 2006): i) formulating the prior probability distributions for targeted parameters, ii) specifying the likelihood function, and iii) MCMC sampling for the posterior probability distributions.

To obtain the prior distribution of targeted parameters E and K in the model, a database of E and K for TN was compiled from the literature. This resulted in 89 records from 22 published studies for E and 139 records from 21 published studies for K (Fig. 2) (see Appendix A). The studies for E were obtained from field plots, small catchments, large watersheds and national scales over the past twenty years. The studies for K were obtained from reach segments, single rivers, and entire river system scales over the past thirty years. Collectively they incorporated a wide range of spatial and temporal scales. According to the K–S test result, both log-transformed E and sqrt-transformed K for TN were conformably fitted with normal probability distributions (Fig. 2).

To specify the likelihood function of E and K, Eq. (1) was incorporated into Eq. (2). The observed stream TN load (L_d^*, kg d^{-1}) is taken as the modeled value with the consideration of random error ε, which is formulated by:

$$L_d^* = L_d + \varepsilon = L_u\exp(-KT) + EA\exp\left(-K\frac{T}{2}\right) + \sum_{i=1}^{n} L_i\exp(-KT_i) + \varepsilon \tag{3}$$

where ε has zero mean and variance of σ^2. The variance σ^2 was assumed to follow a standard non-informative diffuse inverse-Gamma distribution (1.0×10^{-3}, 1.0×10^{3}) (Shen and Zhao, 2010). Then the likelihood function for all observations can be expressed as:

$$P(X/\theta) = \prod_{j=1}^{m} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(L_d - L_d^*)^2}{2\sigma^2}} \tag{4}$$

where $m=72$, the number of observations over the 6 year water quality monitoring period for each catchment of the ChangLe River watershed (Fig. 1). Finally, WinBUGS software (Lunn et al., 2000), which implements MCMC using Gibbs sampling, was used for the Bayesian estimation of E and K in Eq. (1) (see Appendix B).

2.3.3. Posterior simulations of NPS export load, TMDL and RLR

Posterior simulations, based on Bayesian model results for each catchment of the ChangLe River watershed, were performed to understand the uncertainty associated with NPS export load, TMDL, and required load reduction (RLR). The posterior simulation for catchment NPS export load was performed using the posterior area-specific export rate (E) from the Bayesian model for each sampling date and catchment area. Here, TMDL (kg d^{-1}) is defined as the allowable total maximum daily loading that can be exported from the catchment to the stream to meet the required water quality target (i.e., 2.0 mg TN L^{-1}) at the catchment outlet. The TMDL for each sampling date was inversely calculated from Eq. (1) using the maximum daily loads at the upstream node ($L_{u,m}$, kg d^{-1}), downstream node ($L_{d,m}$, kg d^{-1}) and the inlet nodes from tributaries and point sources ($L_{i,m}$, kg d^{-1}). Stream TN loads were calculated by multiplying the target TN concentration by the stream water discharge on the jth day. The posterior TMDL simulation was performed using the posterior in-stream loss rate coefficient (K, d^{-1}) from the Bayesian model results:

$$TMDL = \frac{L_{d,m} - L_{u,m}\exp(-KT) - \sum_{i=1}^{n} L_{i,m}\exp(-KT_i)}{\exp\left(-K\frac{T}{2}\right)}. \tag{5}$$

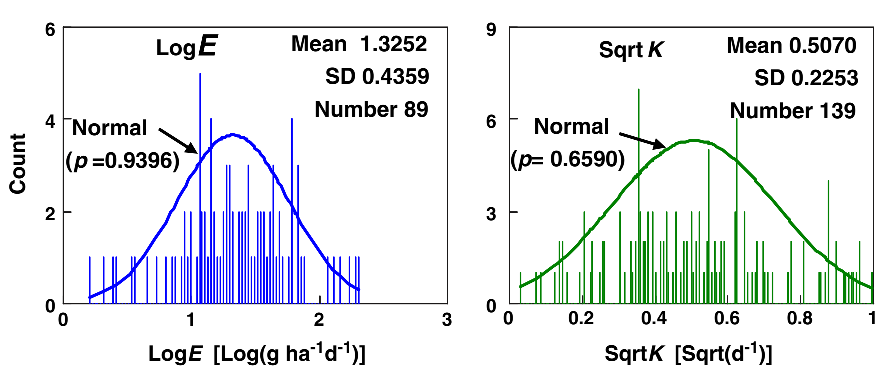

Fig. 2. Histograms of log-transformed area-specific export rates (E) and sqrt-transformed stream loss rate coefficients (K) for total nitrogen obtained from reported measurements in the published literature. The reference sources can be found in the Appendix A.

To further distinguish the contributions of stream flow dilution and assimilation capacities to the TMDL, the dilution capacity (DC) was defined as the estimated TMDL when in-stream loss rate coefficient $K=0$ in Eq. (5) and assimilation capacity was estimated as the difference between the estimated TMDL and DC (Chen et al., 2011a). Next, the posterior simulation for the RLR was calculated as the difference between the catchment NPS export load and TMDL. The catchment NPS export load and TMDL used for posterior simulation of the RLR were derived from the coupled posterior E and K obtained from the Bayesian model results for a particular sampling date.

2.3.4. Variability and uncertainty expressions of NPS export load, TMDL and RLR

To address the variability of posterior catchment export load, TMDL, and required load reduction (RLR) using the load duration curve (LDC) method, the flow duration curve, which was generated from the relationship between the daily stream discharge data for 2004–2009 at sample site S7 (watershed outlet) and its corresponding exceedance percentile, was divided into three regimes (US EPA, 2007), representing high (0–30th percentile), median (30–70th percentile) and low (70–100th percentile) discharge. Then the LDCs for the daily catchment export load, TMDL, and RLR were developed through ranking them with respect to stream discharge to describe their variability (US EPA, 2006). At the same time, the coefficient of variance value for posterior catchment export load, TMDL, and RLR was calculated for each observation date to compare their uncertainties among flow regimes (Shen and Zhao, 2010). Finally, the relationship between posterior RLRs for all observation dates in each flow regime and its corresponding exceedance percentile was developed and the percent exceedance for a particular RLR for each flow regime was used to evaluate the uncertainty of exceeding the TMDL or target in-stream concentration for TN (Bonta and Cleland, 2003). In this study, only posterior total nitrogen NPS export load, TMDL and RLR for the entire ChangLe River watershed were addressed to demonstrate the efficacy of the proposed integrated modeling approach.

3. Results and discussion

3.1. Bayesian calibration

To inversely calibrate area-specific export rate (E) and in-stream loss rate coefficient (K) (Eq. (1)), TN load at the catchment outlet, stream water travel time, and upstream and tributaries inflow loads for each sampling date at each catchment were input into Eq. (4) using WinBUGS. The model successfully converged after 10,000 runs. The first 5000 runs were discarded after model convergence and then a total of 1000 samples for each unknown quantity were randomly taken from the next 5000 iterations as the posterior E and K to reduce autocorrelation (Malve and Qian, 2006).

The Monte Carlo (MC) error (an estimate of the difference between the mean of the sampled values and the true posterior mean), standard deviation (SD), median and the confidence levels at 2.5% and 97.5% for posterior distributions of E and K are summarized in Table 2. These model results show that E and K have small MC errors (<8% of SD), indicating that the model converged well (Lunn et al., 2000). As expected, the calibrated E was negatively correlated with the proportion of woodland ($r=-0.91^{*}$ for average mean E) among the various catchments of the watershed with the highest and lowest E often occurring in the catchment FR and BJ, respectively. However, the calibrated K was negatively correlated with stream discharge ($r=-0.96^{**}$ for average mean K) among the various catchments of the watershed with the highest and lowest K often occurring in the catchment FR and MS, respectively, which are consistent with previous studies (Alexander et al., 2000; Hoos and McMahon, 2009). This is due to a decrease in water-bed contact area per unit water volume, resulting in less TN assimilation per unit TN loading or per water travel time as stream discharge increases (Smith et al., 1997; Alexander et al., 2000; Chen et al., 2011b).

Using the resulting posterior E and K values with the stream water travel time and inflow TN loads from upstream water bodies and tributaries, stream TN loads for each catchment were predicted (Fig. 3). Observed versus modeled results were strongly correlated with more than 92% of the observed data falling within the 95% confidence interval and r^2 values higher than 0.95. Considering the complexities of NPS pollution and in-stream assimilation, and the limits of one-dimensional stream water quality models, the modeled results are very reasonable. Thus the established model can be applied to practical water quality management, especially for small and medium size streams where the assumptions of one-dimension and steady-state for in-stream nutrient processes are valid. For large streams, more complex models, such as a three-dimensional water quality model (Shen et al., 2006), should be adopted to address in-stream nutrient processes. However, these complex models have more parameters and require considerable process-level data for calibration. Further studies are needed to test the efficacy of applying the proposed methodology to more complex models for application in large river systems.

3.2. Catchment TN export to the stream

Fig. 4 illustrates the posterior mean, median, and 2.5% and 97.5% quartiles (95% confidence intervals) of the daily catchment TN export load, corresponding to each sampling date. During the six-year study period (2004–2009), the mean TN export load ranged from 1.0×10^3 to 36.4×10^3 kg d^{-1}. There was remarkable variation for catchment TN export loads, which increased with stream discharge ($r=0.95^{**}$ for mean export load), which is consistent with previous studies that have shown that catchment NPS pollutant loads are mainly dependent on transport by runoff; thus large runoff events transport

Table 2
The posterior area-specific export rate (E, g ha^{-1} d^{-1}) and in-stream loss rate coefficient (K, d^{-1}) for TN in each catchment of the ChangLe River watershed.

Catchments		2.5%	Mean	Median	97.5%	SD	MC error
SY	E	1.18–574	8.51–597	5.26–595	31.6–636	3.90–46.1	0.0035–0.0466
	K	0.013–0.370	0.265–0.623	0.243–0.584	0.571–1.649	0.098–0.450	0.0009–0.0037
BJ	E	2.05–336	9.14–362	7.19–363	31.9–385	4.36–53.5	0.0041–0.0715
	K	0.029–0.219	0.198–0.386	0.163–0.428	0.382–0.819	0.068–0.226	0.0015–0.0025
SH	E	0.84–523	12.3–563	10.8–556	37.5–622	4.26–52.7	0.0124–0.0625
	K	0.015–0.211	0.214–0.431	0.174–0.418	0.448–1.148	0.119–0.302	0.0011–0.0031
CR	E	0.99–580	9.49–617	7.90–618	27.2–662	5.14–39.4	0.0082–0.0585
	K	0.006–0.221	0.145–0.336	0.137–0.339	0.250–0.805	0.078–0.208	0.0008–0.0037
FR	E	2.03–627	16.0–689	12.2–695	45.6–742	7.59–68.0	0.0147–0.0752
	K	0.011–0.344	0.445–0.685	0.385–0.705	1.100–2.720	0.259–0.619	0.00107–0.0034
MS	E	0.623–657	12.0–826	9.70–676	40.1–1129	6.86–187	0.0312–0.0728
	K	0.001–0.069	0.060–0.195	0.021–0.344	0.128–0.537	0.020–0.151	0.0012–0.0022

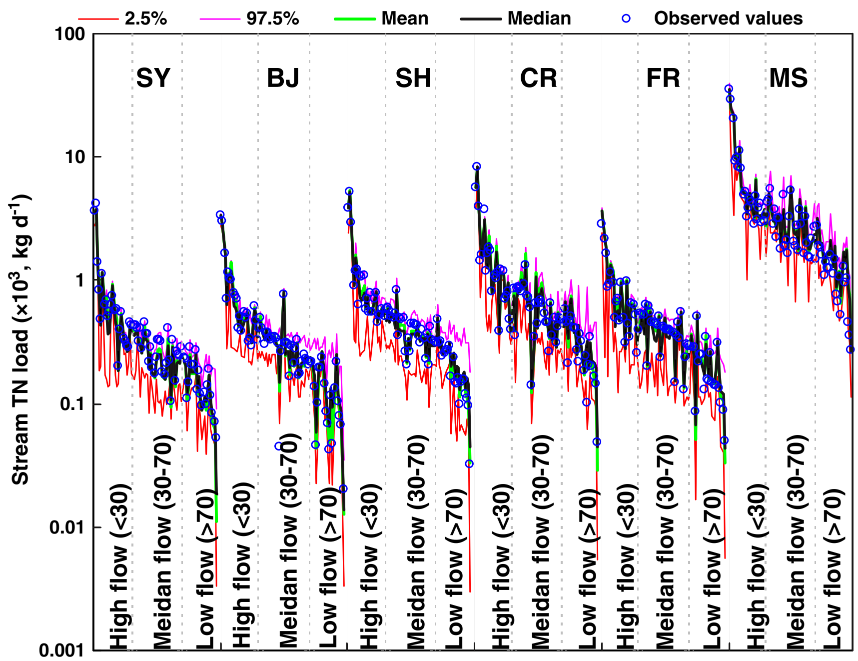

Fig. 3. Model fitting results for TN loads showing observed data versus the modeled mean, median and 2.5% and 97.5% confidence level values for catchments in the ChangLe River watershed.

more pollutants from the watershed resulting in higher NPS export loads (Shen and Zhao, 2010; Chen et al., 2011a). Larger catchment export loads occurred during high flow regimes (about 58% of the total mean annual load) while smaller export loads occurred during low flow regimes (about 5% of the total mean annual load). Thus, variability associated with changing stream discharge is necessary to consider in NPS pollution control and management at the watershed scale.

By solving the mechanistic equation (Eq. (1)) using Bayesian statistics, the resulting posterior area-specific export rate can provide both point and interval estimations for NPS export loads at different flow percentiles. Taking the first catchment export load estimation in Fig. 4 as an example, it can be calculated that the point estimate for the export load is 36.4×10^3 kg d^{-1} (mean value), there is a 0.5 probability that the export load is greater than 35.7×10^3 kg d^{-1} (median), and 95% of the potential values for the export load will fall within the range 17.0×10^3–42.9×10^3 kg d^{-1} (95% confidence interval). This not only quantitatively describes the uncertainty for NPS pollution load estimation, but also provides a confidence level that can be easily understood by decision makers from a management point of view.

The average coefficient of variance for estimated catchment TN export load was ranked: high flow regime > median flow regime > low flow regime (Table 3). This means that the uncertainty of the catchment TN export load exhibits a temporal variability (resulting from stream discharge variability), with greater uncertainty in the high flow regime. This result is due to the fact that the NPS pollution was dominated by variability in runoff processes. Runoff processes during high runoff periods might present higher variability in location, time, and intensity of occurrence, which in turn results in higher uncertainty of runoff nutrient export to the stream (Shen et al., 2008). Therefore, the assumption that NPS TN from the catchment area is entering a stream segment at a site equivalent to one-half the stream length segment (Eq. (1); T/2) is probably not sufficient for characterizing the behavior of TN entering at random locations along a stream segment during the high flow

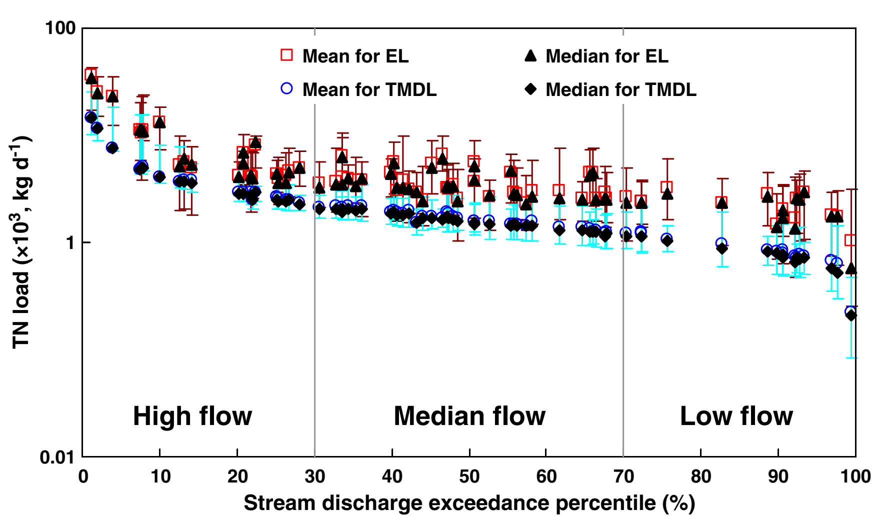

Fig. 4. Catchment NPS export load (EL) and TMDL for TN in different flow regimes of the ChangLe River watershed. The error bars indicate the 95% confidence interval for TN export load and TMDL.

Table 3
Average coefficient of variance (CV) of estimated catchment NPS export load (EL), TMDL and required load reduction (RLR) for TN in each flow regime of the ChangLe River watershed.

Flow regimes	High flow (<30%)	Median (30–70%)	Low flow (>70%)
EL	33.4 ± 13.0%a	30.4 ± 8.6%b	23.5 ± 9.8%c
TMDL	29.1 ± 11.4%a	21.9 ± 7.9%b	15.7 ± 5.8%c
RLR	27.4 ± 15.5%a	16.4 ± 10.1%b	14.1 ± 8.9%c

Small letters denote significant differences ($P<0.05$) among flow regimes.

regime. To lower the uncertainty for NPS export load estimation, it is necessary to obtain observational data from more sampling sites along a stream segment to characterize high discharge regimes.

3.3. Variable TN total maximum daily load

The mean TN TMDL ranged from 0.22×10^3 to 14.8×10^3 kg d^{-1} during the study period (Fig. 4). In general, the TMDL increased with increasing flow ($r = 0.97^{**}$ for mean TMDL) with larger and smaller TMDL values occurring during high and low flow regimes, respectively. This positive relationship results primarily from increases in dilution capacity and in-stream assimilation capacity for TN with increasing stream discharge. With increases in stream discharge, the dilution capacity for TN increased from 0.04×10^3 to 13.8×10^3 kg d^{-1} and mean in-stream assimilation capacity increased from 0.18×10^3 to 0.95×10^3 kg d^{-1} (Fig. 5a). The positive relationship between in-stream assimilation capacity and stream discharge could be due to an increase in the wetted surface area (i.e., increasing stream width) (Chen et al., 2011a), increased opportunity for retention by backwater areas or riparian buffer zones along the stream (Brian et al., 1999; Mulholland et al., 2008; Chen et al., 2010b) and an increase in the nitrogen load available for processing (Saunders and Kalff, 2001; Chen et al., 2011b) as high flows wash more nitrogen from the watershed (Fig. 4). Thus, a temporally variable expression for TMDLs based on river discharge volume is necessary for NPS pollution-dominated watersheds. Environmental managers must take into account both changing assimilation and dilution capacities with stream water discharge when making decisions for TMDL implementation strategies.

Although both dilution and assimilation capacities increased with increasing stream discharge, the dilution capacity from stream discharge accounted for the majority of the TN TMDL (70.8 ± 11.9%), with mean in-stream assimilation capacity contributing 29.2 ± 11.9% (Fig. 5b). Although TN assimilation capacity increased with stream discharge (Fig. 5a), the percentage contribution of the assimilation capacity to the TMDL decreased with increasing stream discharge ($r = -0.95^{**}$ for the mean assimilation capacity contribution percentage). This negative correlation between TN assimilation percentage and stream discharge is partially due to a decrease in the duration time (e.g., T or T_i in Eq. (5)) for different biogeochemical reactions to assimilate TN as stream discharge increasing. Further, it is due to a decrease in in-stream TN loss rate coefficients (K) resulting from a decrease in water-bed contact area per unit water volume as stream discharge increases (Fig. 6). Therefore, compared to the dilution capacity, the assimilation capacity presents a more significant effect on the TMDL during low flow periods as compared to high flow events, which accounted for a comparable proportion of the TMDL in the low flow regime (accounting for more than 40% of the TMDL on average) (Fig. 5b). In the traditional LDC method, however, the TMDL is calculated by multiplying the 50th percentile flow and water quality target for each flow regime (US EPA, 1997), which ignores the effects of in-stream nutrient assimilation capacity on the TMDL. For the ChangLe River watershed, ignoring the in-stream assimilation capacity would underestimate the TMDL by 29.2 ± 11.9%, especially during low flows (>40%, Fig. 5b), which would introduce unnecessarily excessive costs on NPS export load reduction practices.

The average coefficient of variance for the estimated TN TMDL was ranked as follows: high flow regime > median flow regime > low flow regime (Table 3), indicating the greatest uncertainty in the high flow regime. This result is primarily due to the uncertainty in the assimilation capacity, since the dilution capacity was based on actual measurements for stream discharge and TN concentration. During high flow regimes, there are more opportunities for TN retention within the backwater areas or riparian buffer zones and by complex in-stream biogeochemical reactions (such as hyporheic exchange) (Mulholland et al., 2008). Thus the assumption of first-order reaction dynamics for K, steady-state and one dimensional processes for in-stream nutrient fate and the estimated water travel time (e.g., T or T_i in Eq. (5)) may be inefficient in fully describing the complexities of assimilation mechanisms at high flows. Therefore, greater uncertainty is associated with the TN TMDL during periods with high stream discharge.

3.4. Required TN load reduction

When compared with the existing catchment TN export loads or the in-stream TN concentrations (mean = 3.89 ± 1.59 mg L^{-1} at seven sampling sites) for the 6-year study period, the ChangLe River watershed failed to meet the TMDL target level of 2.0 mg L^{-1} for TN. Thus, existing catchment TN export must be reduced to attain the target TN level. Fig. 7 illustrates the posterior mean, median,

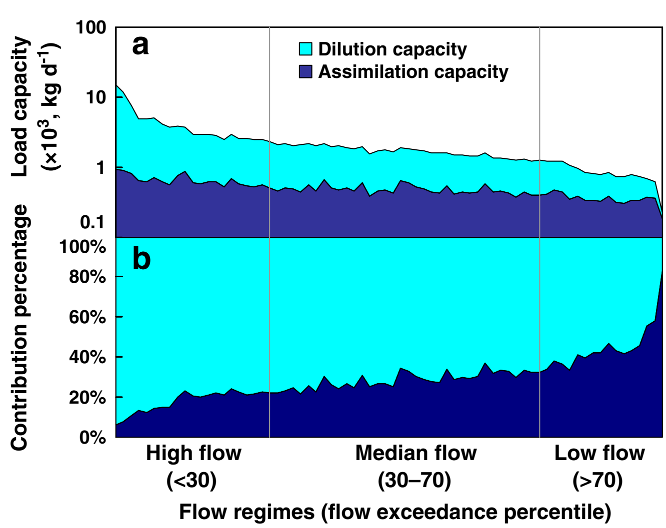

Fig. 5. Contributions of dilution and assimilation capacities to the TN TMDL of the ChangLe River watershed.

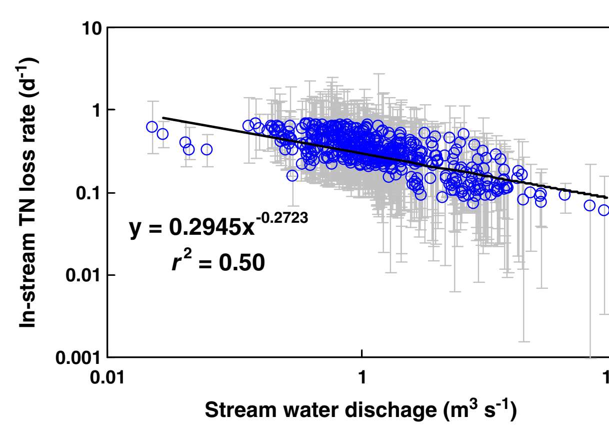

Fig. 6. Relationships between posterior in-stream TN loss rate coefficient (K) and stream discharge in the ChangLe River watershed. The error bars indicate the 95% confidence interval for K. r^2 denotes the coefficient of determination for the regression between stream water discharge and mean K (n = 432).

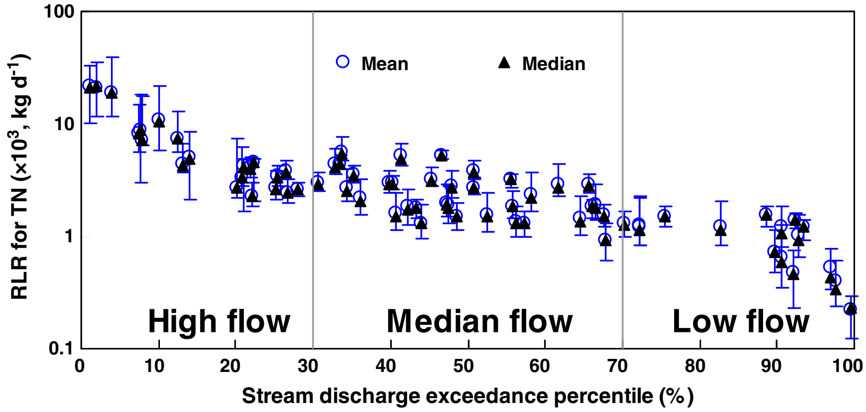

Fig. 7. Required reduction for catchment TN export load (RLR) in different flow regimes for the ChangLe River watershed. The error bars indicate the 95% confidence interval.

and 95% confidence intervals for the required TN export load reduction based on the field monitoring data. During the study period, the mean required load reduction (RLR) ranged from 0.22×10^3 to 21.1×10^3 kg d^{-1}. The RLR increased with increasing stream discharge ($r = 0.95^{**}$ for mean values). This indicates that generation of catchment TN export load was larger than the corresponding TMDL with increasing stream water discharge. Thus, for NPS pollution-dominated watersheds, there needs to be a temporally variable expression (e.g., a function of stream discharge) for determining RLR practices.

The average coefficient of variance for the estimated TN RLR was ranked: high flow regime > median flow regime > low flow regime (Table 3). The higher uncertainty for the RLR in the high flow regime is due to the fact that uncertainties for catchment NPS export and TMDL were both highest in the high flow regime. Due to the temporal variability in uncertainty, caution should be exercised for implementation of load reduction practices in TMDL programs that use an arbitrarily determined margin of safety (representing the uncertainty, Zheng and Keller, 2008), since it might result in unnecessary costs for reduction practices in the low flow regime and insufficient reduction practices to address NPS generation within the high flow regime.

Fig. 8 illustrates the relationship between the RLR and compliance percent of the target stream TN level at different flow regimes. This relationship provides decision makers and stakeholders with an explicit basis for designing load reduction strategies. Traditionally

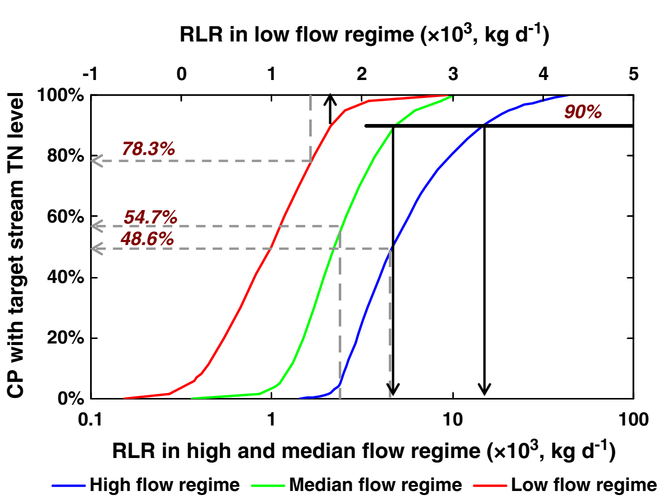

Fig. 8. Relationship between required load reduction (RLR) and compliance percent (CP) for stream water TN concentration in different flow regimes for the ChangLe River watershed. The solid arrows denote the RLR for 90% compliance with the targeted stream water TN concentration; the dashed arrows denote CP with targeted stream water TN concentration for the traditional RLR setting method.

the RLR was set as the difference between the existing load (calculated from the 90th percentile of the measured TN concentration and the flow at the middle of the flow percentile) and the set TMDL corresponding to the median flow for each flow regime (US EPA, 2007). By neglecting the uncertainty when using this set load reduction strategy, it is difficult to assure the desired 90% compliance in the targeted in-stream TN concentration (US EPA, 1997). As shown in Fig. 8, the RLR obtained from the traditional method would only provide 48.6%, 54.7% and 78.3% compliance of the targeted stream TN concentration during high, median and low flow regimes, respectively. To assure 90% compliance with the targeted TN concentration (i.e., 10% possibility of violating the target), the existing NPS TN export loads in this study would need to be reduced 1.7×10^3, 4.6×10^3, and 14.6×10^3 kg d^{-1} in the high, median and low flow regimes, respectively (Fig. 8). It should be pointed out that this load reduction scenario is just one of the many ways to obtain the load reductions. If necessary, we can obtain different RLRs under different confidence levels for water quality compliance according to Fig. 8, which can be used to support the practical adaptive implementation of TMDL programs while fully considering uncertainty factors (Borsuk et al., 2003).

4. Conclusion

The integrated modeling approach developed in this study takes the variability of catchment NPS export load, TMDL and required load reduction (RLR) into consideration, while also addressing the uncertainties associated with their estimations. Both of these aspects are important components in NPS pollution control and watershed management. The integrated modeling approach determines the RLR under different target levels for water quality compliance. Thus this approach can be used to support the practical adaptive implementation of TMDL programs. Since the prior distributions of the targeted parameters (i.e., area-specific NPS export rate and in-stream loss rate coefficient for TN) and WinBUGS software code for this modeling approach are both offered here, the integrated modeling approach is easy to apply. This integrated modeling approach combines the merits but overcomes the shortcomings of receiving stream nutrient load models, Bayesian statistics and the load duration curve method. It provides researchers and managers with a simple but efficient tool to deal with variability and uncertainty issues in TMDL development with limited data requirements.

In the ChangLe River watershed, estimated catchment NPS export load, TMDL and RLR for TN synchronously increased with increasing stream discharge. The uncertainties associated with catchment NPS export load, TMDL and RLR for TN also exhibited a temporal pattern that was greatest for the high flow regime. To assure 90% compliance with the targeted in-stream TN concentration (2.0 mg L^{-1}), the RLR was determined to be 1.7×10^3, 4.6×10^3, and 14.6×10^3 kg TN d^{-1} for the low, median and high flow regimes, respectively. For the NPS pollution-dominated watershed, temporal variability (largely a function of stream discharge) and uncertainty are both necessary considerations for TMDL development.

Supplementary materials related to this article can be found online at doi:10.1016/j.scitotenv.2012.04.042.

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